

PATENT COOPERATION TREATY

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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

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Applicant:

YANG, Chun, Byung et al

1. The designated Office is hereby notified of its election made:



in the demand filed with the International preliminary Examining Authority on:

13 January 2000 (13.01.00)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was



was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
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PATENT COÖPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 99-PCT-010	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/KR 99/00638	International filing date (<i>day/month/year</i>) 23 October 1999 (23.10.1999)	Priority Date (<i>day/month/year</i>) 27 May 1999 (27.05.1999)
International Patent Classification (IPC) or national classification and IPC IPC ⁷ : C08F 4/654, C08F 10/02		
Applicant SAMSUNG GENERAL CHEMICALS CO., LTD. et al.		

- This international preliminary examination report has been prepared by this International Preliminary Examination Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 3 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

- This report contains indications relating to the following items:

- ☒ Basis of the opinion
- ☐ Priority
- ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Lack of unity of invention
- ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Certain documents cited
- ☐ Certain defects in the international application
- ☐ Certain observations on the international application

Date of submission of the demand 13 January 2000 (13.01.2000)	Date of completion of this report 11 May 2001 (11.05.2001)
Name and mailing address of the IPEA/AT Austrian Patent Office Kohlmarkt 8-10 A-1014 Vienna Facsimile No. 1/53424/200	Authorized officer PUSTERER Telephone No. 1/53424/311

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/KR 99/00638

I. Basis of the report

1. With regard to the elements of the international application:*

☒ the international application as originally filed☐ the description:

pages _____, as originally filed

pages _____, filed with the demand

pages _____, filed with the letter of _____.

☐ the claims:

pages _____, as originally filed

pages _____, as amended (together with any statement) under Article 19

pages _____, filed with the demand

pages _____, filed with the letter of _____.

☐ the drawings:

pages _____, as originally filed

pages _____, filed with the demand

pages _____, filed with the letter of _____.

☐ the sequence listing part of the description:

pages _____, as originally filed

pages _____, filed with the demand

pages _____, filed with the letter of _____.

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language _____ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).☐ the language of publication of the international application (under Rule 48.3(b)).☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in printed form.☐ filed together with the international application in computer readable form.☐ furnished subsequently to this Authority in written form.☐ furnished subsequently to this Authority in computer readable form.☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.4. ☐ The amendments have resulted in the cancellation of:☐ the description, pages _____.☐ the claims, Nos. _____.☐ the drawings, sheets/fig _____.5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as „originally filed“ and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/KR 99/00638

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

I. Statement	Novelty (N)	Claims 1-6	YES
		Claims	NO
	Inventive step (IS)	Claims 1-6	YES
		Claims	NO
	Industrial applicability (IA)	Claims 1-6	YES
		Claims	NO

Citations and explanations (Rule 70.7)

Claims 1 to 6 meet the requirements for novelty and inventive step.

Neither of the cited specifications disclose or suggest a catalyst for polymerization or copolymerization of ethylene being produced by preparing a magnesium solution by reacting a halogenated magnesium compound with alcohol, reacting said solution with an ester compound having at least one hydroxy group and a boron compound having an alkoxy group, and reacting then said solution with a mixture of a titanium compound and a silicon compound.

Additionally the claimed application undoubtedly can be industrially applied.

Therefore the subject-matter of claims 1 to 6 satisfies the criterion set forth in Article 33 (2-4) PCT.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 00/73355 A1

(54) Title: A CATALYST FOR ETHYLENE HOMO- AND CO-POLYMERIZATION

(57) Abstract: The present invention relates to a catalyst for homo-polymerization or co-polymerization of ethylene, or more particularly to a solid complex titanium catalyst for homo-polymerization or co-polymerisation of ethylene, said catalyst being produced by preparing a magnesium solution by contact-reacting a halogenated magnesium compound with alcohol, reacting said solution with an ester compound having at least one hydroxy group and a boron compound having an alkoxy group, and then reacting said solution with a mixture of a titanium compound and a silicon compound. The catalyst of the present invention has good activity, and the polymers produced by means of the catalyst herein has advantages in that the polymers have high bulk density with narrow particle distribution and a reduced amount of fines particles.

A CATALYST FOR ETHYLENE HOMO- AND CO-POLYMERIZATION

5 Technical Field

The present invention relates to a catalyst for homo-polymerization or co-polymerization of ethylene, or more particularly to a good-activity titanium solid complex catalyst supported in a carrier containing magnesium, said catalyst being capable of producing polymers of high bulk density with a narrow particle distribution and low contents of fine particles.

10

Background of the Invention

Catalysts containing magnesium for polymerization or co-polymerization of ethylene are known to have very good catalytic activities and to accord good bulk density, which are suitable for liquid phase or gas phase polymerization. By liquid phase polymerization of ethylene, it denotes the polymerization process performed in such medium of bulk ethylene, isopentane, or hexane, and as for the important characteristics of the catalyst used in the process, they are as follows: high activity, bulk density, the amount of molecules of low molecular weight dissolved in a medium, particle distribution of polymers, the amount of fine particles, and so on.

20 Many of the titanium-based catalysts containing magnesium for olefin polymerization, and the manufacturing methods thereof have been reported. Especially, many processes making use of magnesium solutions to obtain olefin polymerization catalysts of good bulk density have been known. There is a means of obtaining a magnesium solution by reacting magnesium compounds with such electron donors as alcohol, amine, cyclic ether, or organic carboxylic acid
25 in the presence of a hydrocarbon solvent. As for the cases of use of alcohol, they are disclosed in US Patent Nos. 4,330,649, and 5,106,807. Further, the methods for production of catalysts containing magnesium by reacting a magnesium solution with a halogenated compound such as titanium tetrachloride are well known. Such catalysts provide good bulk density, but there is much yet to be improved with respect to their catalytic activity and bulk density. Meanwhile,
30 when the polymerization is carried out by means of using such catalysts, the resultant polymers have large amounts of fine powder with a broad particle size distribution and low bulk density. As such, there are serious defects with respect to productivity and handling at the time of

processing.

To solve these problems, US Patent Nos. 3,953,414 and 4,111,835 disclosed a process for making catalysts for production of globular polymers with a very large average particle size by means of spray-drying magnesium dichloride hydrates. These processes, however, require much production facilities for catalysts such as spray-drying equipment and others, and the resultant catalysts have the disadvantages of low activities. Further, due to the existence of very large particles in polymers, there may arise problems at the time of the melting process.

10 Summary of the Invention

As shown above, there is a need for the development of a new catalyst for homopolymerization or copolymerization of ethylene for producing polymers with the following conditions: simple manufacturing process, high polymerization activity, high bulk density for polymers by means of controlling the catalyst particles, and in particular narrow particle distribution with few fine particles. In the present invention, therefore, it is intended to provide a method for producing, from low-cost compounds via a simple process, a catalyst having an excellent catalytic activity, capable of producing polymers of high bulk density with narrow particle distribution and few fine particles. Further, the specific production process of catalysts and the steps thereof as disclosed in the present invention have never been reported in the prior art.

Consequently, the objective of the present invention is to provide a catalyst for homopolymerization or copolymerization of ethylene, said catalyst having good catalytic activity, capable of producing polymers of high bulk density, with narrow particle distribution and few fine particles.

Another objective of the present invention is to provide a simple process for producing a catalyst for homopolymerization or copolymerization of ethylene.

30 Still other objectives and the utility of the present invention will become bulk as references are made with respect to the following descriptions and the claims thereto.

Detailed Description of the Preferred Embodiments

The catalyst of good catalytic activity, capable of producing polymers having narrow particle distribution and high bulk density with few fine particles as provided in the present invention, is produced by a simple yet efficient manufacturing process, which comprises (i) preparing a magnesium solution by contact-reacting a halogenated magnesium compound with an alcohol, (ii) reacting the same with an ester compound containing at least one hydroxy group and a boron compound containing an alkoxy group, and (iii) producing a solid titanium catalyst by adding a titanium compound and a silicon compound.

Types of halogenated magnesium compounds used in the present invention are as follows: di-halogenated magnesiums such as magnesium chloride, magnesium iodide, magnesium fluoride, and magnesium bromide; alkylmagnesium halides such as methylmagnesium halide, ethylmagnesium halide, propylmagnesium halide, butylmagnesium halide, isobutylmagnesium halide, hexylmagnesium halide, amylmagnesium halide; alkoxy-magnesium halides such as methoxymagnesium halide, ethoxymagnesium halide, isopropoxymagnesium halide, butoxymagnesium halide, octoxymagnesium halide; and aryloxymagnesium halides such as phenoxymagnesium halide and methyl-phenoxymagnesium halide. Of the above magnesium compounds, two or more compounds can be used in a mixture. Further, the above magnesium compounds can be effectively used in the form of a complex compound with other metals.

20

Of the compounds listed above, some can be represented by a simple formula, but the others cannot be so represented depending on the production methods of magnesium compounds. In the latter cases, it can be generally regarded as a mixture of some of the listed compounds. For example, the following compounds can be used in the present invention: such compounds obtained by reacting magnesium compounds with polysiloxane compounds, silane compounds containing halogen, ester, or alcohol; and such compounds obtained by reacting magnesium metals with alcohol, phenol, or ether in the presence of halosilane, phosphorus pentachloride, or thionyl chloride. However, the preferable magnesium compounds are magnesium halides, especially magnesium chloride or alkylmagnesium chloride, preferably those having an alkyl group of 1~10 carbons; alkoxy-magnesium chlorides, preferably those having 1~10 carbons; and aryloxymagnesium chlorides, preferably those having 6~20 carbons. The magnesium solution used in the present invention is made by dissolving the aforementioned compounds with

alcohol as a solvent in the presence or absence of a hydrocarbon solvent.

As to the types of hydrocarbon solvents used in the present invention, they include aliphatic hydrocarbons such as pentane, hexane, heptane, octane, decane, and kerosene; alicyclic hydrocarbons such as cyclobenzene, methylcyclobenzene, cyclohexane, and methylcyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene, ethylbenzene, cumene, and cymene; and halogenated hydrocarbons such as dichloropropane, dichloroethylene, trichloroethylene, carbon tetrachloride, and chlorobenzene.

When a magnesium compound is converted into a magnesium solution, alcohol is used in the presence or absence of the aforementioned hydrocarbons. The types of alcohol include those containing 1 ~ 20 carbon atoms such as methanol, ethanol, propanol, butanol, pentanol, hexanol, octanol, decanol, dodecanol, octadecyl alcohol, benzyl alcohol, phenylethyl alcohol, isopropyl benzyl alcohol, and cumyl-alcohol, although alcohols containing 1 ~ 12 carbon atoms are preferable. The average size of a target catalyst and its particle distribution can vary according to the type of alcohol, the total contents, types of magnesium compounds, and the ratio of magnesium to alcohol, etc. Nevertheless, the total amount of alcohol required to obtain the magnesium solution is at least 0.5 mol per each mole of the magnesium compound, preferably about 1.0 ~ 20 mol, or more preferably about 2.0 ~ 10 mol.

20

The reaction of a magnesium compound with alcohol for producing magnesium solution is preferably carried out in the presence of hydrocarbon. The reaction temperature, while variable depending on the type and the amount of alcohol, is at least -25°C, preferably -10 ~ 200°C, or more preferably about 0 ~ 150°C. It is preferable to carry out the reaction for about 15 minutes ~ 5 hours, preferably for about 30 minutes ~ 4 hours.

25

Of the electron donors used in the present invention, the ester compounds containing at least one hydroxy group include unsaturated aliphatic acid esters having at least one hydroxy group such as 2-hydroxy ethylacrylate, 2-hydroxy ethylmethacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropylmethacrylate, 4-hydroxy butylacrylate, pentaerithritol triacrylate; aliphatic monoesters or polyesters containing at least one hydroxy group such as 2-hydroxy ethyl acetate, methyl 3-hydroxy butylate, ethyl 3-hydroxy butylate, methyl 2-hydroxy isobutylate, ethyl 2-

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hydroxy isobutylate, methyl 3-hydroxy-2-methyl propionate, 2,2-dimethyl-3-hydroxy propionate, ethyl-6-hydroxy hexanoate, t-butyl-2-hydroxy isobutylate, diethyl-3-hydroxy glutarate, ethyl lactate, isopropyl lactate, butyl isobutyl lactate, isobutyl lactate, ethyl mandelate, dimethyl ethyl tartrate, ethyl tartrate, dibutyl tartrate, diethyl citrate, triethyl citrate, ethyl-2-hydroxy-caproate, diethyl bis-(hydroxy methyl)malonate; aromatic esters having at least one hydroxy group such as 2-hydroxy ethyl benzoate, 2-hydroxy ethyl salicylate, methyl-4-(hydroxy methyl) benzoate, methyl-4-hydroxy benzoate, ethyl-3-hydroxy benzoate, 4-methyl salicylate, ethyl salicylate, phenyl salicylate, propyl-4-hydroxy benzoate, phenyl-3-hydroxy naphthanoate, monoethylene glycol monobenzoate, diethylene glycol benzoate, triethylene glycol benzoate; alicyclic esters having at least one hydroxy group such as lactone, and others. The amount of the ester compound containing at least one hydroxy group should be 0.001 ~ 5 mol per mole of magnesium, or preferably 0.01 ~ 2 mol per mole of magnesium.

For the boron compound containing an alkoxy group, the other electron donor in the present invention, a compound having a general formula of $BR^1_n(OR^2)_{3-n}$ (here, R^1 represents a hydrocarbon having 1 ~ 20 carbons or a halogen element, R^2 for a hydrocarbon having 1 ~ 20 carbons, and n for an integer of 0 ~ 2) is preferable. More specifically, it includes trimethyl borate, triethyl borate, tributyl borate, triphenyl borate, methylboron diethoxide, ethylboron diethoxide, ethylboron dibutoxide, butylboron dibutoxide, phenylboron phenoxide, diethylboron ethoxide, dibutylboron ethoxide, diphenylboron phenoxide, diethoxyboron chloride, diethoxyboron bromide, diphenoxyboron chloride, ethoxyboron dichloride, ethoxyboron dibromide, butoxyboron dichloride, phenoxyboron dichloride, and ethylethoxyboron chloride. The amount of such compound should be 0.005 ~ 3 mol per mole of magnesium, or more preferably 0.05 ~ 2 mol per mole of magnesium.

As for the temperature for the contact-reaction of a magnesium solution, an ester compound containing at least one hydroxy group, and an alkoxy boron compound, the temperature of 0 ~ 100 °C is appropriate, or more preferably 10 ~ 70 °C.

In the process, the catalyst particles are recrystallized by reacting the magnesium compound solution with a mixture of a liquid titanium compound of a general formula of $Ti(OR)_aX_{4-a}$ (R stands for an alkyl group with 1 ~ 10 carbons; X for a halogen atom; and "a" for a

natural number of 0 to 4) and a silicon compound of a general formula of R_nSiCl_{4-n} (here R stands for hydrogen; or an alkyl, alkoxy, haloalkyl, or aryl group having 1 to 10 carbons; or a halosilyl or halosilyl alkyl group having 1 to 8 carbons; $n = 0-3$). The types of titanium compounds which satisfy the general formula of $Ti(OR)_aX_{4-a}$ include 4-halogenated titanium such as $TiCl_4$, $TiBr_4$, and TiI_4 ; 3-halogenated alkoxy-titanium such as $Ti(OCH_3)Cl_3$,
5 $Ti(OC_2H_5)Cl_3$, $Ti(OC_2H_5)Br_3$, and $Ti(O(i-C_4H_9)Br_3$; 2-halogenated alkoxy-titanium compounds such as $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$, $Ti(O(i-C_4H_9)_2Cl_2$, and $Ti(OC_2H_5)_2Br_2$; and tetra-alkoxy titaniums such as $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, and $Ti(OC_4H_9)_4$. A mixture of the above titanium compounds can also be used in the present invention. However, the preferable titanium
10 compounds are those containing halogen, or more preferably titanium tetrachloride.

The types of silicon compounds satisfying the above general formula of R_nSiCl_{4-n} include silicon tetrachloride; trichlorosilanes such as methyltrichlorosilane, ethyltrichlorosilane, phenyltrichlorosilane; dichlorosilanes such as dimethylchlorosilane, diethyldichlorosilane, di-
15 phenyldichlorosilane, and methylphenyldichlorosilane; monochlorosilanes such as trimethylchlorosilane; and a mixture of these silicon compounds can also be used in the present invention, or more preferably silicon tetrachloride can be used.

The amount of the mixture of a titanium compound and a silicon compound used during
20 the re-crystallization of the magnesium compound solution is appropriately 0.1 ~ 200 mol per mole of the halogenated magnesium compound, preferably 0.1 ~ 100 mol, or more preferably 0.2 ~ 80 mol. The molar ratio of a titanium compound to a silicon compound in the mixture is appropriately 0.05 ~ 0.95, or more preferably 0.1 ~ 0.8. When the magnesium compound solution is reacted with the mixture of a titanium compound and a silicon compound, the shape
25 and the size of the resultant re-crystallized solid constituents vary a great deal according to the reaction conditions. In order to obtain the target size of the catalyst, and the size and distribution of the polymers, as intended by the present invention, it is advantageous to maintain the above mixture amounts for said titanium and silicon compounds, as well as their mix ratios. If it is outside of the above range, it will be difficult to obtain the results as intended. The reaction of
30 the magnesium compound with the mixture of a titanium compound and a silicon compound should be carried out preferably at a sufficiently low temperature to result in formation of solid constituents. More preferably, the reaction should be carried out by contact-reaction at -70 ~

70°C, or most preferably at -50 ~ 50°C. After the contact-reaction, the reacting temperature is slowly raised for sufficient reaction for the duration of 0.5 ~ 5 hours at 50 ~ 150°C.

The particles of the solid catalysts obtained during the above process can be further reacted with titanium compounds. These titanium compounds are titanium halides, and halogenated alkoxy titanium with an alkoxy functional group of 1 ~ 20 carbons. At times, a mixture of these compounds can also be used. Of these compounds, however, titanium halide and a halogenated alkoxy titanium compound having an alkoxy functional group of 1~8 carbons can be appropriately used, or more preferably titanium tetrahalide can be used.

10

Further, the solid complex titanium catalysts produced during the process of the present invention can be utilized during homo-polymerization or co-polymerization of ethylene. In particular, the catalyst is used in homo-polymerization of ethylene, and also in co-polymerization of ethylene and α -olefin such as propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, or 1-hexene having three or more carbons.

15

The polymerization reaction in the presence of the catalyst of the present invention is carried out by means of using (i) a solid complex titanium catalyst of the present invention, comprising magnesium, titanium, halogen, and electron donors, and (ii) a cocatalyst comprising compounds of organic metals of Groups II and III of the Periodic Table.

20

The solid complex titanium catalyst constituents of the present invention can be used in pre-polymerization of ethylene or α -olefin prior to the use in the aforementioned polymerization reaction. The pre-polymerization can be carried out in the presence of a hydrocarbon solvent such as hexane, at a sufficiently low temperature, with ethylene or α -olefin under pressure, in the presence of the above catalyst constituents and such an organic aluminum compound as triethylaluminum. Pre-polymerization, by maintaining the shape of the catalyst by surrounding the catalyst particles with polymers, is helpful in producing good-quality post-polymerization shape of the polymers. The weight ratio of the polymers to the catalysts after pre-polymerization is ordinarily 0.1 : 1 to 20 : 1.

30

The organometallic compound in the present invention can be represented by a general formula of MR_n , wherein, M stands for a metal constituent of Group II or IIIA in the Periodic Table, such as magnesium, calcium, zinc, boron, aluminum, and gallium, R for an alkyl group with 1 ~ 20 carbons, such as a methyl, ethyl, butyl, hexyl, octyl, or decyl group, and n for the atomic value of the metal constituent. As for more preferable organometallic compounds, trialkyl aluminum having an alkyl group of 1 ~ 6 carbons, such as triethylaluminum and triisobutylaluminum, or the mixture thereof can be utilized. On occasions, an organic aluminum compound having one or more halogen or hydride groups, such as ethylaluminum dichloride, diethylaluminum chloride, ethyl-aluminum sesqui-chloride, or diisobutylaluminum hydride can also be used.

As for the polymerization reaction, it is possible to carry out either gas phase or bulk polymerization in the absence of an organic solvent, or liquid slurry polymerization in the presence of an organic solvent. These polymerization methods, however, are carried out in the absence of oxygen, water, or other compounds that may act as catalytic poison.

The concentration of the solid complex titanium compound (i) with respect to the polymerization system, in the case of a liquid phase slurry polymerization, is approximately 0.001 ~ 5 mmol in terms of the titanium atom of the catalyst per one liter of the solvent, or more preferably approximately 0.001 ~ 0.5 mmol. As for the solvent, the following compounds or the mixtures thereof can be used: alkanes or cycloalkanes such as pentane, hexane, heptane, n-octane, isooctane, cyclohexane, methylcyclohexane; alkylaromatic such as toluene, xylene, ethylbenzene, isopropylbenzene, ethyltoluene, n-propylbenzene, diethylbenzene; and halogenated aromatics such as chlorobenzene, chloronaphthalene, ortho-dichlorobenzene.

In the case of gas phase polymerization, the amount of the solid complex titanium catalyst (i) should be approximately 0.001 ~ 5 mmol in terms of the titanium atom of the catalyst per one liter of the polymerization reactant, preferably approximately 0.001 ~ 1.0 mmol, or more preferably approximately 0.01 ~ 0.5 mmol.

The preferable concentration of the organometallic compound (ii) is about 1 ~ 2,000 mol, as calculated by the aluminum atoms, per mole of the titanium atoms in the catalyst (i), or more

preferably about 5 ~ 500 mol.

To secure a good reaction rate of polymerization, the polymerization herein is carried out at a sufficiently good temperature, regardless of the polymerization manufacturing process.

5 Generally, the temperature of approximately 20 ~ 200°C is appropriate, or more preferably approximately 20 ~ 95°C. The appropriate pressure of monomers at the time of polymerization is the atmospheric to 100 atm, or more preferably 2 ~ 50 atm.

10 In the present invention, the changes in the molecular weight according to the amount of hydrogen at the time of polymerization are shown as a melt index (ASTM D 1238), the index generally known in the art. The value of the melt index generally becomes greater as the molecular weight decreases.

15 The products obtained by the method of polymerization of the present invention are solid ethylene homogeneous polymers or the copolymers of ethylene and α -olefin, which have excellent bulk density and fluidity. Since the polymer yields are sufficiently good, there is no need for the removal of the catalyst residues.

20 The present invention is further described by means of the examples and comparative examples as below but should not be confined or limited to these examples.

Example 1

Production of catalyst

25 A solid complex titanium catalyst was produced by means of the following three steps:

(i) Step : Production of magnesium solution

30 Into a 1.0L reactor equipped with a mechanical stirrer, replaced with nitrogen atmosphere, 9.5 g of $MgCl_2$ and 400 ml of decane were placed therein. After they were stirred at 300 rpm, 60 ml of 2-ethyl hexanol was added thereto. The temperature was

raised to 120°C, and then the reaction was allowed to continue for three hours. The homogenous solution, which was obtained after the reaction, was cooled to room temperature (25 °C).

- 5 (ii) Step : Contact-reaction of a magnesium solution, an ester containing a hydroxy group and an alkoxy boron compound

To the magnesium solution, cooled to room temperature as above, 1.2 ml of 2-hydroxyethyl methacrylate and 5.1 ml of trimethyl borate were added, and then the
10 reaction was allowed to continue for an hour.

- (iii) Step : Treatment of a mixture of a titanium compound and a silicon compound

Into the above solution, a solution mixture of 30 ml of titanium tetrachloride and 30
15 ml of silicon tetrachloride was dripped thereto for one hour at room temperature (25 °C). After the completion of the dripping process, the temperature of the reactor was raised to 80 °C while stirring, after which was maintained at that temperature for one hour. After stopping the stirring, the supernatant of the solution was removed, and to the remaining solid layer was added 300 ml of decane and 100 ml of titanium tetrachloride in sequence.
20 There, the temperature was raised to 100 °C and maintained thereat for two hours. After the reaction, the reactor was cooled to room temperature and the washing of the resulting solid product with 400ml of hexane was repeated until the removal of free unreacted titanium chloride. The titanium content of the solid catalyst so produced was 3.8 %.

25 Polymerization

A 2-L good-pressure reactor was dried in an oven and assembled while still hot. In order to make the inside of the reactor nitrogen atmosphere, nitrogen and vacuum were alternatively manipulated three times in the reactor. To the reactor was added 1,000 ml of n-hexane, after which 2 mmols of triethylaluminum and a solid catalyst by 0.03 mmol in terms
30 of the titanium atoms were added thereto. Then, 500 ml of hydrogen was added. The temperature was raised to 80 °C while stirring at 700 rpm. The pressure of ethylene was

adjusted to 80 psi, and the polymerization was allowed to continue for an hour. After the polymerization, the temperature of the reactor was lowered to room temperature, and a large amount of ethanol was added to stop the polymerization. The polymer thus produced was collected by separation and was dried in an oven at 50°C for at least six hours, whereby
5 polyethylene was obtained in the form of white powder.

The polymerization activity (kg of polyethylene divided by mmol of Ti) was calculated as the weight (kg) ratio of the polymers as produced per the amount of the catalysts so used (mmol of Ti). The results of the polymerization are shown in Table 1, together with the bulk
10 density (g/ ml) of the polymers, the melt index (g/10 minutes), and particle size distribution of the polymers.

Example 2

15 In Step (ii) of Example 1, 1.2 ml of 2-hydroxyethyl methacrylate and 7.7 ml of trimethyl borate were used for the production of the catalyst. The titanium content of the catalyst thus produced was 3.4 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

20 Example 3

In Step (ii) of Example 1, 1.2 ml of 2-hydroxyethyl methacrylate and 7.6 ml of triethyl borate were used for the production of the catalyst. The titanium content of the catalyst thus produced was 3.5 %. The polymerization was carried out as in Example 1, and the results
25 thereof are shown in Table 1.

Example 4

In Step (ii) of Example 1, 1.2 ml of 2-hydroxyethyl methacrylate and 11.4 ml of triethyl
30 borate were used for the production of the catalyst. The titanium content of the catalyst thus produced was 3.4 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 5

In Step (ii) of Example 1, 1.2 ml of 2-hydroxyethyl methacrylate and 12.1 ml of tributyl borate were used for the production of the catalyst. The titanium content of the catalyst thus produced was 3.9 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 6

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In Step (ii) of Example 1, 1.2 ml of 2-hydroxyethyl methacrylate and 18.2 ml of tributyl borate were used for the production of the catalyst. The titanium content of the catalyst thus produced was 3.5 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

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Example 7

In Step (ii) of Example 1, 1.2 ml of 2-hydroxyethyl methacrylate and 11.4 ml of triethyl borate were used, and in Step (iii) 40 ml of titanium tetrachloride and 20 ml of silicon tetrachloride were used for the production of the catalyst. The titanium content of the catalyst thus produced was 4.0 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

Example 8

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In Step (ii) of Example 1, 1.2 ml of 2-hydroxyethyl methacrylate and 11.4 ml of triethyl borate were used, and in Step (iii) 20 ml of titanium tetrachloride and 40 ml of silicon tetrachloride were used for the production of the catalyst. The titanium content of the catalyst thus produced was 3.3 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

30

Comparative Example 1

In Step (ii) of Example 1, the catalyst was produced without using 2-hydroxyethyl methacrylate or trimethyl borate. The titanium content of the catalyst thus produced was 3.9 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

5

Comparative Example 2

In Step (ii) of Example 1, 1.2 ml of 2-hydroxyethyl methacrylate was used alone, without trimethyl borate, for the production of the catalyst. The titanium content of the catalyst thus produced was 3.3 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

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Comparative Example 3

In Step (ii) of Example 1, neither 2-hydroxyethyl methacrylate nor trimethyl borate was used, and in Step (iii) 60 ml of titanium tetrachloride was used for the production of the catalyst. The titanium content of the catalyst thus produced was 4.1 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

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Comparative Example 4

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In Step (ii) of Example 1, 1.2ml of 2-hydroxyethyl methacrylate and 12.1ml of tributyl borate were used, and in Step (iii) 60 ml of titanium tetrachloride was used for the production of the catalyst. The titanium content of the catalyst thus produced was 3.7 %. The polymerization was carried out as in Example 1, and the results thereof are shown in Table 1.

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Table 1 Results of Polymerization

Example	Activity (kg PE/ mmol Ti)	Bulk density (g/ml)	Melt Index (g/10min)	Distribution of Polymer Particles (wt%)							
				>1100 μm	840 μm	500 μm	250 μm	177 μm	105 μm	74 μm	<44 μm
1	5.4	0.38	0.52	0.6	3.4	10.8	52.4	21.2	8.4	2.6	0.6
2	4.8	0.36	0.43	0.4	9.4	16.4	45.2	18.7	6.7	3.2	0
3	6.3	0.40	0.58	0.2	1.2	12.6	58.2	24.8	2.6	0.4	0

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4	5.9	0.38	0.42	0.3	4.6	9.3	54.8	19.8	6.7	4.5	0
5	6.4	0.37	0.54	0.8	4.6	8.6	59.4	18.6	7.1	0.9	0
6	5.4	0.36	0.52	0.5	4.1	10.5	52.8	20.2	11.7	0.7	0
7	6.2	0.35	0.54	0.2	0.7	16.4	41.4	36.8	1.2	2.1	1.2
8	6.0	0.35	0.52	1.2	12.1	26.2	38.4	19.4	1.5	0.4	0.8
CE 1	3.8	0.29	0.31	0	0.6	0.5	7.6	13.9	24.2	36.2	17.0
CE 2	4.4	0.26	0.42	2.2	2.7	2.4	9.4	13.7	12.6	34.2	22.8
CE 3	3.9	0.22	0.36	1.6	0.4	1.2	8.6	15.5	38.7	19.4	14.6
CE 4	3.6	0.28	0.31	0.7	3.8	5.1	16.2	32.4	22.1	15.5	4.2

* CE : Comparative Examples

As shown above, the production process of the catalyst of the present invention for homo-polymerization and co-polymerization of ethylene is simple with excellent catalytic activity. Further, the polymers so produced have high bulk density and narrow particle distribution in addition to having the effect of reducing the amount of fine particles.

Claims

What is claimed is:

- 5 1. A solid titanium catalyst for homo-polymerization and co-polymerization of ethylene, wherein said catalyst is produced by:
- (i) preparing a magnesium compound solution by contacting a halogenated magnesium compound with alcohol;
- 10 (ii) reacting said solution with an ester compound having at least one hydroxy group and a boron compound having an alkoxy group; and
- (iii) reacting the solution from above(ii) with a mixture of a titanium compound and a
- 15 silicon compound to produce solid catalyst, and optionally the solid catalyst are further reacted with a titanium compound.
2. A solid titanium catalyst according to Claim 1, wherein said ester compound having at least one hydroxy group is an unsaturated aliphatic acid ester having at least one hydroxy group,
- 20 which is selected from the group consisting of 2-hydroxy ethylacrylate, 2-hydroxy ethylmethacrylate, 2-hydroxy propyl acrylate, 2-hydroxy propylmethacrylate, 4-hydroxy butylacrylate, pentaerithritol triacrylate; an aliphatic monoester or polyester having at least one hydroxy group, which is selected from the group consisting of 2-hydroxy ethyl acetate, methyl 3-hydroxy butylate, ethyl 3-hydroxy butylate, methyl 2-hydroxy isobutylate, ethyl 2-
- 25 hydroxy isobutylate, methyl 3-hydroxy-2-methyl propionate, 2,2-dimethyl-3-hydroxy propionate, ethyl-6-hydroxy hexanoate, t-butyl-2-hydroxy isobutylate, diethyl-3-hydroxy glutarate, ethyllactate, isopropyl lactate, butyl-isobutyl lactate, isobutyl lactate, ethyl mandelate, dimethyl ethyl tartrate, ethyl tartrate, dibutyl tartrate, diethyl citrate, triethyl citrate, ethyl-2-hydroxy-caproate, diethyl *bis*-(hydroxymethyl) malonate; an aromatic ester having
- 30 at least one hydroxy group, which is selected from the group consisting of 2-hydroxy ethyl benzoate, 2-hydroxy ethyl salicylate, methyl-4-(hydroxy methyl) benzoate, methyl-4-hydroxy benzoate, ethyl-3-hydroxy benzoate, 4-methyl salicylate, ethyl salicylate, phenyl

- salicylate, propyl-4-hydroxy benzoate, phenyl-3-hydroxy naphthanoate, monoethylene glycol monobenzoate, diethylene glycol benzoate, triethylene glycol monobenzoate; and an alicyclic ester having at least one hydroxy group as in hydroxy butyl-lactone; and wherein said boron compound having an alkoxy group is represented by the general formula of $BR^1(OR^2)_{3-n}$, where R^1 represents a hydrocarbon having 1 ~ 20 carbons or a halogen atom, R^2 for a hydrocarbon having 1 ~ 20 carbons, and n for an integer of 0 ~ 2, said boron compound being selected from the group consisting of trimethyl borate, triethyl borate, tributyl borate, triphenyl borate, methylboron diethoxide, ethylboron diethoxide, ethylboron dibutoxide, butylboron dibutoxide, phenylboron diphenoxide, diethylboron ethoxide, dibutylboron ethoxide, diphenylboron phenoxide, diethoxyboron chloride, diethoxyboron bromide, diphenoxyboron chloride, ethoxyboron dichloride, ethoxyboron dibromide, butoxyboron dichloride, phenoxyboron dichloride, and ethylethoxyboron chloride.
3. A solid titanium catalyst according to Claim 1, wherein said titanium compound is represented by the general formula of $Ti(OR)_aX_{4-a}$, where R stands for an alkyl group with 1 ~ 10 carbons, X for a halogen atom, and "a" for an integer of 0 to 4; and wherein said silicon compound is represented by the general formula of R_nSiCl_{4-n} , where R stands for hydrogen, or an alkyl, alkoxy, haloalkyl, or aryl group having 1 to 10 carbons; or a halosilyl or halosilyl alkyl group having 1 to 8 carbons; n = an integer of 0 to 4.
4. A solid titanium catalyst according to Claim 3, wherein said titanium compound is a 4-halogenated titanium, which is selected from the group consisting of $TiCl_4$, $TiBr_4$, and TiI_4 ; a 3-halogenated alkoxy titanium, which is selected from the group consisting of $Ti(OCH_3)Cl_3$, $Ti(OC_2H_5)Cl_3$, $Ti(OC_2H_5)Br_3$, and $Ti(O(i-C_4H_9))Br_3$; a 2-halogenated alkoxy titanium, which is selected from the group consisting of $Ti(OCH_3)_2Cl_2$, $Ti(OC_2H_5)_2Cl_2$, $Ti(O(i-C_4H_9))_2Cl_2$, and $Ti(OC_2H_5)_2Br_2$; and a tetralkoxy titanium, which is selected from the group consisting of $Ti(OCH_3)_4$, $Ti(OC_2H_5)_4$, and $Ti(OC_4H_9)_4$; and wherein said silicon compound is a silicon tetrachloride; a trichlorosilane such as methyltrichlorosilane, ethyltrichlorosilane, and phenyl-trichlorosilane; a dichlorosilane such as dimethylchlorosilane, diethyldichlorosilane, diphenyldichlorosilane, and methylphenyldichlorosilane; and a monochlorosilane such as trimethylchlorosilane.

5. A solid titanium catalyst according to Claim 3, wherein said titanium compound is titanium tetrachloride, and said silicon compound is silicon tetrachloride.
6. A solid titanium catalyst according to Claim 1, wherein the amount of the mixture of a titanium compound and a silicon compound is 0.1 ~ 200 mol per mole of said halogenated magnesium compound, and the molar ratio of said titanium compound to said silicon compound in the mixture is 0.05 ~ 0.95.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR99/00638

A. CLASSIFICATION OF SUBJECT MATTER		
IPC ⁷ : C 08 F 4/654, C 08 F 10/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC ⁷ : C 08 F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
EPODOC, PAJ, WPI		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5459116 A (Ro et al.) 1995.10.17 The whole document	1-6
A	US 5438110 A (Ishimaru et al.) 1995.08.01 Example 3	1-6
A	EP 668296 A1 (Mitsui Petrochemical Industries, Ltd.) 1995.08.23 Claims 4 & 5; page 8, line 57 - page 9, line 2; comparative example 4	1-6
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: „A“ document defining the general state of the art which is not considered to be of particular relevance „E“ earlier application or patent but published on or after the international filing date „L“ document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) „O“ document referring to an oral disclosure, use, exhibition or other means „P“ document published prior to the international filing date but later than the priority date claimed „T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention „X“ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone „Y“ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art „&“ document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
6 December 1999 (06.12.99)		29 March 2000 (29.03.00)
Name and mailing address of the ISA/AT Austrian Patent Office Kohlmarkt 8-10; A-1014 Vienna Facsimile No. 1/53424/200		Authorised officer Pusterer Telephone No. 1/53424/331

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR 99/00638

Patent document cited in search report			Publication date	Patent family member(s)			Publication date
US	A	5459116	17-10-1995	CN	A	1099041	22-02-1995
				CN	B	1041097	09-12-1998
				JP	A2	7149813	13-06-1995
				JP	B2	2680262	19-11-1997
				KR	B1	123016	12-11-1997
US	A	5438110	01-08-1995	US	A	4990479	05-02-1991
				AT	E	102223	15-03-1994
				CA	A1	1338088	27-02-1996
				CN	A	1225369	11-08-1999
				DE	C0	68913375	07-04-1994
				DE	T2	68913375	01-06-1994
				EP	A2	350170	10-01-1990
				EP	A3	350170	27-03-1991
				EP	B1	350170	02-03-1994
				ES	T3	2052004	01-07-1994
				JP	A2	2229807	12-09-1990
				JP	B2	2723138	09-03-1998
				KR	B1	9202488	26-03-1992
				JP	A2	2084404	26-03-1990
				JP	B2	2723137	09-03-1998
				CN	A	1040379	14-03-1990
				CN	B	1043233	05-05-1999
EP	A1	668296	23-08-1995	CA	AA	2142748	19-08-1995
EP	B1	668296	06-05-1998	CA	C	2142748	23-02-1999
				CN	A	1126728	17-07-1996
				CN	B	1039494	12-08-1998
				DE	C0	69502312	10-06-1998
				DE	T2	69502312	08-10-1998
				JP	A2	7278221	24-10-1995
				KR	B1	162685	15-01-1999

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 4363-4003PC	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
International application No. PCT/US02/08706	International filing date (<i>day/month/year</i>) 21 March 2002 (21.03.2002)	(Earliest) Priority Date (<i>day/month/year</i>) 21 March 2001 (21.03.2001)
Applicant BIOARRAY SOLUTIONS, LTD		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 4 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the Report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (See Box II).

4. With regard to the title,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the abstract,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No. 1



as suggested by the applicant.



None of the figures



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/08706

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---	US 5,015,452 A (MATJEVIC) 14 May 1991 (14.05.1991) all.	1-35
Y		----- 1-35
X ---	US 6,120,666 A (JACOBSON et al) 19 September 2000 (19.09.2000); all.	1-35
Y		----- 1-35
X ---	US 5,308,586 A (FRITSCHKE et al) 3 May 1994 (03.05.1994); all.	1-2
Y		----- 1-2
X ---	US 6,136,171 A (FRAZIER et al) 24 October 2000 (24.10.2000); all.	1-35
Y		----- 1-35

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/08706

Continuation of B. FIELDS SEARCHED Item 3:

EAST

search terms: light, control, electrokinetic, fractionate, particle

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under Article 19. The Notes are based on the requirements of the Patent Cooperation Treaty and of the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule" and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions, respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the letter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended ?

The claims only.

The description and the drawings may only be amended during international preliminary examination under Chapter II.

When ? Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments ?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How ? Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

What documents must/may accompany the amendments ?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confounded with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/08706

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : B01D 57/02, 59/42, 59/50, 61,58; C02F 1/469; C08F 2/58; C25B 15/00, 7/00; G01F 1/64; G01L 1/20, 9/18; G01N 27/26 US CL : 204/450, 600		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 204/450, 600 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Please See Continuation Sheet		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---	US 6,132,685 A (KERCSO et al) 17 October 2000 (17.10.2000) column 1, lines 38-57; column 5, line 51 - column 6, line 22; column 7 line 7 - column 18, line 26.	1 -----
Y		2
X ---	US 6,251,691 B1 (SEUL) 26 June 2001 (26.06.2001) all. Same Inventor as Applicant.	1-35 -----
Y		1-35
X,P ---	US 6,358,387 B1 (KOPF-SILL et al) 19 March 2002 (19.03.2002); Figure 7A, 7B, 13, 14, 15; all.	1-2 -----
Y,P		1-35
X,P ---	US 6,387,707 B1 (SEUL et al) 14 May 2002 (14.05.2002); all. Same Inventor as Applicant.	1-35 -----
Y,P		1-35
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents:		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
30 May 2002 (30.05.2002)	08 JUL 2002	
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703)305-3230	Authorized officer Jill A. Warden TELEPHONE 308-0661 Telephone No. (703) 308-0661	